

# POLYPROPYLENE REINFORCED WITH GLASS BEADS. PREDICTION OF INTERFACE ADHESION BY IGC.

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**SUMMARY:** It's well known that material's adhesion is the result of several phenomena of mechanical and physicochemical character, these last ones rely on the interactions between atoms or molecules in the surface of the materials in contact. So, to approach the adhesion problems it is necessary to have a good knowledge of the surfaces and their characteristics. Inverse Gas Chromatography (IGC) has proved to be a powerful tool for characterising the surface energy of solid materials. IGC can determinate the surface capability of *interaction with non-polar compounds* and its *acidic or basic character, its affinity to functional groups*. There are several methods described in the literature for the evaluation of surface characteristics by IGC.

Polypropylene is an attractive thermoplastic material because of its low price, good processability and recyclability, but it presents serious adhesion problems with coatings and reinforcements.

In this work, the surface characterisation of several polypropylenes in terms of surface free energy is measured by IGC: *non-polar character, acid and basic character and affinity to OH groups*. The same is done on glass beads, without or with surface modification. Calculations are made of the interaction (energy per surface unit) between the possible matching materials. Some specimens are prepared with the available material, and some mechanical testing is done.

**KEYWORDS:** Reinforced Polypropylene, Glass-Polypropylene Interface, Inverse Gas Chromatography, Surface Properties, and Surface Modification.

## INTRODUCTION

Many technical and industrial problems today, depend on interface interactions. That is the case of reinforcement-matrix interaction control in all types of composite materials, or the compatibility of coatings with the substrate when protective layers must be applied to sensitive materials, or the effectiveness of adhesives, etc.

It's well known that material's adhesion is the result of several phenomena of mechanical and physicochemical character, this last one rely on the interactions between atoms or molecules in the surface of the materials in contact. So, to approach the adhesion problems it is necessary to have a good knowledge of the surfaces and their characteristics.

Inverse Gas Chromatography (IGC) has proved to be a powerful tool for characterising the surface energy of solid materials. By IGC it can be measured the surface capability of *interaction with non-polar compounds* and its *acidic or basic character, its affinity to*

*aromatic rings, OH groups, etc.* There are well accepted methods described in the literature<sup>1,2</sup> for the determination of the non-polar component of the free energy in a surface (London Component) and also several methods described for the evaluation of the acid or basic characteristics<sup>3,4,5,6</sup> (Specific Interactions). A new method has been recently proposed for the determination of the polar character of the surfaces<sup>7</sup>.

In this paper two polypropylene copolymers, one with no fillers and the other with filler and an added polymer, have been evaluated by IGC. Two types of glass beads, one as received and the other with a surface modification, have been evaluated, as well, by IGC. Interactions are calculated of the matching couples. These measurements and calculated interactions must be checked with some mechanical or physical characteristics of the materials.

Specimens are prepared of the two copolymers filled with both kinds of beads and the materials have been tested in a dynamomechanic analyser, to measure their viscoelastic properties. Results are given and the correlation between calculated interactions, and the mechanical testing results

## THEORY

### Polar and non-polar character of the surfaces

Gas Chromatography is an easy technique of separation and/or identification of solutes in a mixture, based on the fact that, each solute has a *particular* interaction with the stationary phase, and therefore, the different solutes travel through the column, carried by an inert gas, at different rates. The solutes come out of the column separately and the retention volume,  $V_R$ , of each solute, depends on different parameters, among others, the nature of the stationary phase and the nature of the solute. IGC takes advantage of this fact, by using a series of solutes (probes), of well known physicochemical characteristics. Introducing them into the column, and measuring their  $V_R$ , valuable information of the nature of the column can be obtained. The column is built with the fibre or the resin to be studied. When adsorption takes place at infinite dilution, only interactions between probes and the surface of the stationary phase occur, Henry's law can be applied, and  $V_R$  is practically independent of the probe concentration.<sup>8-9</sup> Fowkes<sup>10</sup> proposes to split the interaction energy between a gas and a solid surface in two terms

$$W_A = W_A^D + W_A^{SP} \quad (1)$$

$W_A^D$  including the weak dispersive interactions and  $W_A^{SP}$  including the other types of interactions mainly polar, like acid-base, hydrogen bonding,  $\pi$  bonding etc. The free energy of adsorption,  $-\Delta G_A$ , as a first approximation, can be linked with the work of adhesion  $W_A$  as follows

$$-\Delta G_A = N * a * W_A \quad (2)$$

where  $N$  is Avogadro's number and  $a$  is the area of the probe. Also the free energy of adsorption is related to the  $\ln$  of the retention volume accordingly to

$$\Delta G_A = -R T \ln V_R + K \quad (3)$$

When n-alkanes are employed as probes, the work of adhesion is dominated by dispersive interactions at the interface, eq. 3 is reduced to  $W_A = W_A^D$ , and according to Fowkes's expression<sup>11</sup>:

$$W_A = 2 (\gamma_s^d \gamma_L^d)^{1/2} \quad (4)$$

where  $\gamma_L^d$  is the dispersive component of the free energy of the adsorbate and in the case of n-alkanes, the free energy and  $\gamma_s^d$  is the London component of the solid surface free energy.

The retention volumes of n-alkanes will give information about the ability of the solid surface of interacting with non-polar material, the. In this paper we use the method of Gray, corrected according to Gutierrez et al.<sup>7</sup> where  $\gamma_{CH_2}$ , is calculated by plotting  $a(\gamma_L^d)^{1/2}$  versus number of carbon atoms of the series of n-alkanes. The slope of the line gives us a value of 36.71 mJ/m<sup>2</sup> for  $\gamma_{CH_2}$ . When polar molecules are injected in the column other interactions besides the dispersive ones, take place between the polar molecules (probes) and the material in the column. The total  $V_R$  obtained for each polar probe comes from two types of interactions with the solid surface, as seen in expression (3).  $\Delta G_A$  must be split in two terms, one including the *dispersive interaction* and the other with the *specific interaction*.

In this paper the method of Gutierrez et al.<sup>7</sup> is used for the splitting of the total adsorption energy of the polar probes and the estimation of the *specific interaction*. According to this method the specific interaction is calculated through the measurements of the *shift of CH<sub>2</sub> indexes*,  $I(CH_2)$ , of the polar probes, where

$$I(CH_2) = (I_{K\acute{o}vats} + 100) / 100 \quad (5)$$

The method proposed by our laboratory, allows to compare quite accurately the effect of the modifications in the characteristics of a surface, if we take for the calculations, as reference, the indexes of the polar probes obtained in the unmodified material.

The chosen polar probes for the evaluation of the acid or basic character of the solid stationary phase are volatile molecules like: benzene, chloroform, acetone, ethyl acetate, diethyl ether, methylene chloride, tetrahydrofuran etc. Their electronic donor and acceptor character is found in the literature<sup>12</sup> as DN values and AN values. DN values, measure the energy of a co-ordinate bond between a donor atom and the Sb of SbCl<sub>5</sub>, its value is expressed in kcal/mol. AN is derived from relative <sup>31</sup>P NMR chemical shifts in Et<sub>3</sub>PO, when dissolved in the acid species being evaluated, and is a dimensionless number. Riddle and Fowkes<sup>13</sup>, made corrections of Gutmann's original AN values. But if AN and DN values are not normalised to the same scale, the results of acid- base interactions would turn out to be meaningless. This is done according to Mukhopadhyay<sup>14</sup>, through the DN value of Et<sub>3</sub>PO (the AN reference molecule) that is 40 kcal/mol. DN values can be recalculated in a dimensionless scale, or AN values in kcal/mol. The acid-base interaction, in most papers, and also in this one, use the expression

$$I_{sp} = (K_{a\ s}) DN_{probe} + (K_{b\ s}) AN_{probe} \quad (6)$$

where  $K_{a\ s}$  and  $K_{b\ s}$  are related to the acid or basic character of the solid stationary phase. These constants can be obtained plotting  $I_{sp}/AN$  of each polar probe, versus DN/AN. The slope being  $K_{a\ s}$ , and  $K_{b\ s}$  the intercept.

The adhesion ( $W_A^D$ ) between the polymers and glass beads is calculated with Fowkes expression eq. (4).

The adhesion ( $W_A^{SP}$ ) between the polymers and glass beads is also calculated with a linear expression like equation (6):

$$W_A = (K_{a\ polymer}) (K_{b\ beads}) + (K_{b\ polymer}) (K_{a\ beads}) \quad (7)$$

### **Interaction of the surfaces with OH groups: Hydrogen bonding**

The hydrogen bond (H bond) is the term given to the relatively weak secondary interaction between a hydrogen atom bound to an electronegative atom and another atom, generally also electronegative, which has one or more lone pairs and can thus act as a base. The generalised representation of it can be



The main proton donors are N-H, O-H and F-H. The acceptor atoms can be N, O, F, Cl, Br, I, S or P, but carbon never acts as an acceptor other than in certain  $\pi$  systems. The H bonding can be considered as part of  $W_A^{SP}$  of eq. (1). Injecting a series of 1 alcohols (R-OH) as probes, the specific interaction can be calculated, and as the difference between the members of the series is  $n CH_2$ , a line is obtained when plotting this interaction versus the number of C-H bonds in the group R (see Fig. 1). From the intercept of this line, the interaction of an -OH group with the column material can be obtained. The units given in this paper are J/mol-OH. This magnitude can give us information about the abundance of *electronegative donors* in the surface.

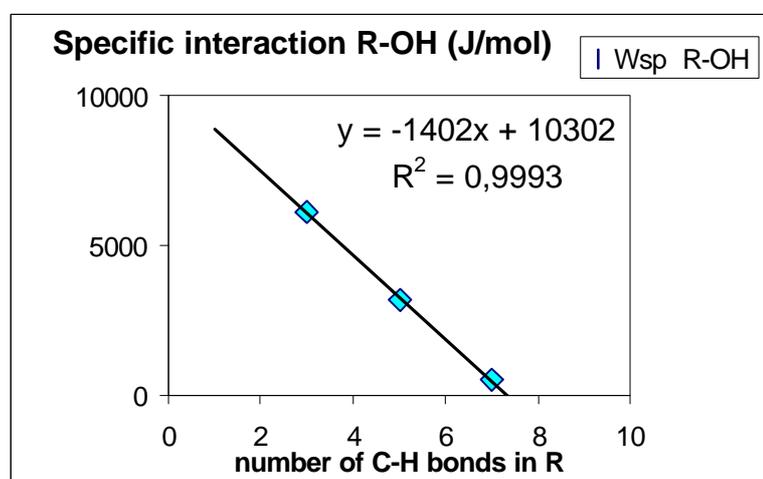


Fig. 1. Specific interaction of methanol, ethanol and propanol with a sample

## EXPERIMENTAL

The instrument used is a Perkin Elmer Autosystem with flame ionisation detector (FID) in the highest sensitive scale. The amount of probes injected is 0.01 to 0.05  $\mu$ l of gas, taken of the headspace of the vessels, to be sure of working in infinite dilution conditions. The carrier gas is helium and the flow rates are variable from 3 to 30 ml/min for each sample/column studied. Dead volume  $V_M$  is calculated mathematically by fitting through progressive approximations the times of release of the series of n-alkanes to an exponential equation  $t_i = f(n)$  where  $t_i$  are the times taken by each alkane to come out of the column and  $n$  is the  $n^\circ$  of carbons. The time due to the dead volume,  $t_m$ , is calculated for  $n$  equal to zero. All the columns are tested at 80°C except treated glass beads that are tested at 40°C.

The dynamic mechanical measurements were carried out on a Rheometrics Dynamic Analyser RDA II. The measuring system is rectangular torsion. The samples used in these studies were rectangular bars of 10 mm x 20 mm of cross-section and 2 mm of thickness. The frequency applied was 10 rad/s during a temperature ramp from 40°C to 100°C at a rate of 5°C/min. The data given are obtained from the curves by interpolation at 60°C in all cases.

## Materials

- Glass beads:* G1 glass beads 106  $\mu\text{m}$  diameter unmodified (SIGMA G-8893)  
 G2 glass beads 106  $\mu\text{m}$  diameter modified (SIGMA G-8893)  
*Polypropylenes:* PP1 PP copolymer (TARGOR IBERICA S.A.)  
 PP2 PP with talcum and EPDM (TARGOR IBERICA S.A.)

The product used for surface modification of the glass beads was 3-aminopropyl-triethoxysilane. Surface modification was carried out in situ on a column packed with glass beads, by injecting a large excess of the coupling agent into the column at 90°C. The column was kept at 90°C for 3 hours under helium flow to remove the excess product and leave homogeneously treated substrate.

All materials were introduced in Teflon tubing of 1/4" outer diameter between 1.5–2 m long for their characterisation by IGC. Before each measurement, the columns were conditioned by heating during 12 hours under helium flow.

## RESULTS AND DISCUSSION

### London Component of samples studied

In Table I, the London Component of the surface energy are given for the four studied materials, calculated by the method of Gray corrected as indicated before, and by the method of Schultz.

**Table I. London Components of the samples in mJ/m<sup>2</sup>**

Sample	Gray corrected ref. 7 (mJ/m <sup>2</sup> )	Schultz ref.2 (mJ/m <sup>2</sup> )
PP copolymer	69.1	73.3
PP +EPDM+talcum	68.9	73.1
Unmodified beads	44.8	47.5
Modified beads	36.1	38.3

According to this the non-polar interaction in the four possible systems made with polymer-glass beads is:

System:	Non-polar interaction (mJ/m <sup>2</sup> )	
	Method ref.2	Method ref.7
Copolymer- unmodified beads	118	111
Copolymer- modified beads	106	100
PP+EPDM+talcum- unmodified beads	118	111
PP+EPDM+talcum- modified beads	106	100

### Acid and basic character of samples studied

In Table II we can see Ka and Kb for three methods of the four samples calculated in mJ/m<sup>2</sup> by the methods of ref.2 and 7.

**Table II. Acid and basic character of the samples in mJ/m<sup>2</sup>**

Sample	Method ref. 2		Method ref.7	
	Ka	Kb	Ka	Kb
PP copolymer	0.13	0.48	0.49	2.40
PP +EPDM+talcum	0.09	0.18	0.40	2.00
Unmodified beads	1.37	0.31	1.37	0.76
Modified beads	0.41	2.15	0.13	1.48

According to this the acid-base interaction in the four possible systems made with polymer-glass beads is:

System:	Acid-base interaction (mJ/m <sup>2</sup> )	
	Method ref. 2	Method ref. 7
Copolymer- unmodified beads	0.69	3.64
Copolymer- modified beads	0.47	1.02
PP+EPDM+talcum- unmodified beads	0.27	3.02
PP+EPDM+talcum- modified beads	0.25	0.83

### Interaction with –OH groups of the samples studied

In Table III, the values of specific interaction with –OH groups of the different materials are given:

**Table III. Interaction of the samples with –OH groups in kJ/mol**

Sample	OH interaction in kJ/mol of OH
PP copolymer	10
PP +EPDM+talcum	10
Unmodified beads	51
Modified beads	14

### Viscoelastic properties of the four systems prepared

In Table IV, the test results obtained in the Dynamic Analyser are given. Elastic module, G' in dyne/cm<sup>2</sup> and the % increase of these module when the two polymers are filled with 25% wt of unmodified and modified glass beads.

**Table IV. Elastic module (G') in the different materials in dyne/cm<sup>2</sup>**

Sample	G'x 10 <sup>9</sup>	Δ G' (%)
PP copolymer	3.1	0
Copolimer+25% unmodified beads	2.8	-12
Copolimer+25% modified beads	2.2	-30
PP +EPDM+talcum	3.6	0
PP+EPDM+talcum +25% unmodified beads	2.8	-23
PP+EPDM+talcum +25% modified beads	2.6	-27

### Discussion

A change should be expected in the storage modulus, G', of the polypropylene polymers when mixed with a material such as glass beads. A decrease in G' is observed in both types of polymers when a material is formed with a 25% wt content of beads. This decrease should be

of the same order when using unmodified or unmodified glass beads, *if the surface modification did not affect the viscoelastic properties of the final material*, but a clear difference is observed of the decrease of  $G'$  when using the two surface-different glass beads as it can be seen in Table IV, which we impute to different adhesion at the interface.

In Table V the calculated interface interactions by IGC are given in  $\text{mJ}/\text{m}^2$ , both the non-polar interaction and the acid-base one for each material prepared:

N°	System	Non-polar interaction	Acid-base interaction	Total
1	Copolymer+25% unmodified beads	111	3.64	115
2	Copolymer+25% modified beads	100	1.02	101
3	PP+EPDM+talcum +25% unmodified beads	111	3.02	114
4	PP+EPDM+talcum +25% modified beads	100	0.83	100

A correlation is found between the calculated interface interactions and the decrease in  $G'$  in the four materials prepared as can be observed in Fig. 2.

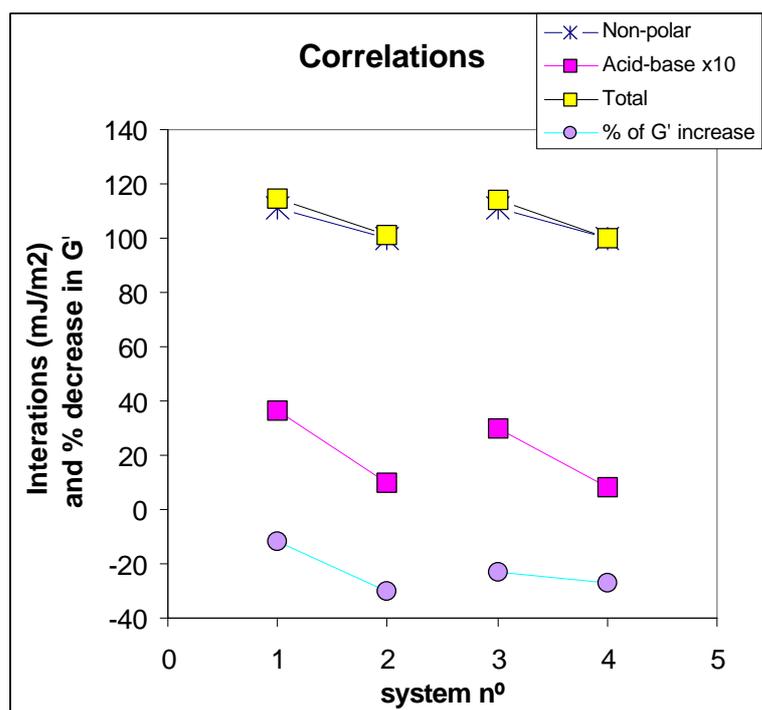


Fig. 2. Correlation between theoretical calculations and mechanical test results.

It is interesting to note that untreated glass beads show higher adherence than the modified ones, and also, the interaction with  $-\text{OH}$  groups is also remarkably higher with the surface of the untreated glass .

## CONCLUSIONS

1. Two polymeric materials are characterised in their surface by IGC methods. Two types of glass beads are also characterised in the same way. Hypothetical interactions are calculated

between the combination of the two polymers and the two types of beads.

2. Four materials are made by mixing the two polymeric materials and a 25% wt. Of the two types of glass beads. Determination of the viscoelastic properties of the four materials is done by testing them in a Dynamic Analyser.

3. Correlation is found between the calculated interface interactions and some viscoelastic test results.

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